Environmental Pollution 171 (2012) 199–206

Contents lists available at SciVerse ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

# Warm season chloride concentrations in stream habitats of freshwater mussel species at risk

Aaron K. Todd*, M. Georgina Kaltenecker

*Environmental Monitoring and Reporting Branch, Ontario Ministry of the Environment, 125 Resources Road, Etobicoke, Ontario M9P 3V6, Canada*

A R T I C L E I N F O

*Article history:*
Received 22 December 2011
Received in revised form
2 June 2012
Accepted 25 July 2012

*Keywords:*
Chloride
Surface water
Streams
Road salt
Freshwater mussels

A B S T R A C T

Warm season (May–October) chloride concentrations were assessed in stream habitats of freshwater mussel species at risk in southern Ontario, Canada. Significant increases in concentrations were observed at 96% of 24 long-term (1975–2009) monitoring sites. Concentrations were described as a function of road density indicating an anthropogenic source of chloride. Linear regression showed that 36% of the variation of concentrations was explained by road salt use by the provincial transportation ministry. Results suggest that long-term road salt use and retention is contributing to a gradual increase in baseline chloride concentrations in at risk mussel habitats. Exposure of sensitive mussel larvae (glochidia) to increasing chloride concentrations may affect recruitment to at risk mussel populations.



## 1. Introduction

Increasing chloride concentrations attributable to road salt (sodium chloride) use have been observed in rivers and streams (herein referred to collectively as streams) in northeastern North America (Rosenberry et al., 1999; Godwin et al., 2003). Stream water chloride concentrations have been related to percent impervious surface, road density and other measures of urban development (Rhodes et al., 2001; Cunningham et al., 2009; Daley et al., 2009) prompting concern for the salinization of freshwater resources with increasing road coverage and road salt use (Kaushal et al., 2005).

Mass balance and modelling studies estimate that 40–77% of the chloride from road salt applied in a given year can be retained in a watershed (Novotny et al., 2009; Perera et al., 2010) and that chloride accumulated in soils and groundwater can be stored for months or years (Bastviken et al., 2006; Bester et al., 2006). Sub-surface accumulation of chloride can contribute to long-term increases in baseline salinity of surface waters (Kelly et al., 2008). Retention and delayed transport of chloride in the environment can also prolong the duration of exposure of aquatic species to elevated chloride, potentially overlapping with sensitive life stages (Findlay and Kelly, 2011).

* Corresponding author.
*E-mail address:* Aaron.Todd@ontario.ca (A.K. Todd).

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http://dx.doi.org/10.1016/j.envpol.2012.07.040

Freshwater mussels, specifically their larval (glochidial) life stage, are especially sensitive to chloride compared to other freshwater organisms (Canadian Council of Ministers of the Environment (CCME), 2011). Freshwater mussels are among the most imperilled groups of animals in the United States and Canada (Williams et al., 1993). Stream habitats in the lower Great Lakes drainage basin of southern Ontario contain the richest assemblage of freshwater mussels in Canada (Metcalfe-Smith et al., 1998), including several species that are classified as endangered under federal species at risk legislation. The basin is also Canada's most road-dense region where over one million tonnes of chloride are applied annually as road salt (Morin and Perchanok, 2003). Most (>60%) of the chloride in the basin's streams is attributable to road salt application (Mayer et al., 1999). Gillis (2011) suggested that stream water chloride concentrations in the basin may pose a threat to successful mussel reproduction. Chloride was found to be a significant factor influencing mussel species richness (Metcalfe-Smith et al., 2003); however, a robust examination of stream water chloride conditions and trends in at risk mussel habitats has not been published.

Freshwater mussels have a complicated life cycle. Female mussels release glochidia from a brooding chamber into the water column to undergo a period of parasitism on a vertebrate host. Chloride and other aquatic contaminants can potentially limit survival of free glochidia or their ability to attach to a host, ultimately affecting recruitment to the mussel population (Cope et al., 2008). In Ontario, glochidia are released between May and October (warm season) depending on species-specific temperature cues (Gillis, 2011) and road salt is generally applied between November and April (cold season). The offset in the timing of glochidia release and road salt application would seem to favour mussel reproduction; however, it is possible that retention and delayed transport of chloride from road salt application in the cold season is exposing sensitive mussel glochidia to elevated chloride concentrations in the warm season.

This paper explores spatial, seasonal and long-term trends in chloride concentrations in stream habitats of mussel species at risk in southern Ontario, with particular emphasis on warm season results. Three questions are addressed.

1. Is there a relationship between land uses and chloride concentrations in mussel habitats?
2. When and how frequently do elevated chloride concentrations occur in mussel habitats?
3. Are concentrations in mussel habitats changing over time and at what rate?

It is hoped that the results will inform ongoing efforts to mitigate the environmental impacts of road salt use and to conserve at risk mussel populations.

## 2. Materials and methods

### 2.1. Monitoring sites

Locations of stream water quality monitoring sites (Ontario Ministry of the Environment (OMOE), 2011) were overlaid on the distribution of mussel species at risk in southern Ontario (Fisheries and Oceans Canada, 2011) using a geographic information system. Twenty-four long-term (25 or more years of monitoring) and independent stream water quality monitoring sites were identified within at risk mussel habitats (Fig. 1). The contributing drainage area of each site was delineated using digital elevation models and watershed attributes, including road density, population density and land cover, were quantified using available geospatial data layers (Table 1). Road density was calculated as the total length of road in the watershed, irrespective of the number of lanes, divided by the watershed area. Population density was estimated from the proportion of each census region (dissemination area) that overlapped with the study watershed. The nearest stream flow monitoring gauge to each site was identified and stream flow data were obtained from Environment Canada (2011).

### 2.2. Chloride data

Stream water chloride concentrations were measured approximately monthly at each site as part of the Provincial Water Quality Monitoring Network. Stream water samples were collected across a range of stream flow conditions, from base to storm flow, and delivered to the OMOE laboratory for analysis. Chloride concentrations were determined by reaction with mercuric thiocyanate, releasing thiocyanate through the sequestration of mercury by the chloride ion to form unionized mercuric chloride. The liberated thiocyanate then reacts with the ferric ion to form ferric thiocyanate, the absorbance of which is measured colourimetrically using a spectrophotometer. The detection limit of this method is 1 mg Cl $L^{-1}$ (OMOE, 2010). Sampling at some sites began in 1964; however, this study is limited to the period 1975–2009 when the laboratory methods and detection limit for chloride analysis were relatively consistent. Corsi et al. (2010) note that continuous- and event-based monitoring strategies are needed to fully characterize the influence of road salt on stream water quality (e.g. Meriano et al., 2009; Perera et al., 2009). Results presented in this study may underestimate the full range of stream water chloride concentrations given that monitoring was not designed specifically to capture periods of road salt runoff.

### 2.3. Data analyses

Chloride data were divided into warm (May–October) and cold (November–April) seasons. Statistical analyses were completed using SYSTAT version 13 with

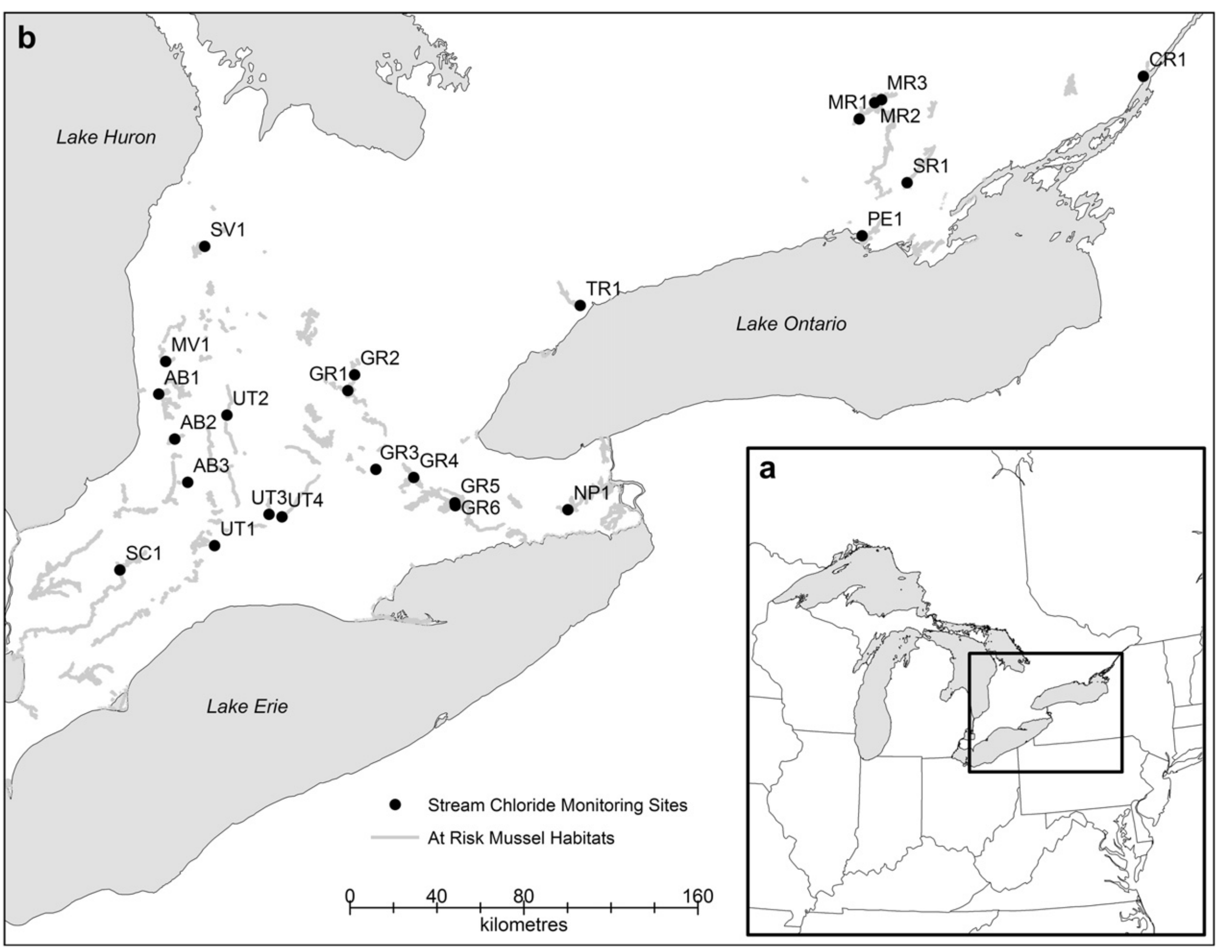


**Fig. 1.** (a) Inset map showing the study area in southern Ontario, Canada; and (b) Locations of the 24 stream water chloride monitoring sites in habitats of mussel species at risk.

**Table 1**
Locations and watershed attributes for the 24 study sites.

| Site # | Stream | Latitude (°N) | Longitude (°W) | Area ($km^2$) | Population density (people $km^{-2}$) | Road density (km $km^{-2}$) | Mean flow ($m^3$ $s^{-1}$) | Agriculture (%) | Forest (%) | Urban (%) |
|---|---|---|---|---|---|---|---|---|---|---|
| AB1 | Bayfield River | 43.551 | −81.589 | 463 | 20 | 1.9 | 6.2 | 89.5 | 8.6 | 0.4 |
| AB2 | Ausable River | 43.362 | −81.509 | 112 | 15 | 2.1 | 1.6 | 88.8 | 8.6 | 1.2 |
| AB3 | Little Ausable River | 43.181 | −81.448 | 143 | 19 | 2.1 | 1.7 | 93.2 | 5.5 | 0.0 |
| CR1 | Lyn Creek | 44.525 | −75.805 | 107 | 25 | 1.6 | 1.5 | 25.6 | 41.3 | 0.0 |
| GR1 | Conestogo River | 43.525 | −80.514 | 818 | 27 | 2.4 | 10.1 | 82.0 | 10.8 | 0.1 |
| GR2 | Grand River | 43.588 | −80.471 | 1153 | 30 | 2.0 | 14.5 | 69.0 | 16.3 | 0.4 |
| GR3 | Nith River | 43.192 | −80.383 | 1126 | 45 | 2.3 | 11.5 | 85.3 | 11.1 | 0.2 |
| GR4 | Fairchild Creek | 43.149 | −80.172 | 388 | 129 | 3.1 | 3.6 | 68.4 | 17.5 | 2.9 |
| GR5 | McKenzie Creek | 43.034 | −79.950 | 174 | 14 | 1.8 | 1.8 | 54.3 | 31.5 | 0.0 |
| GR6 | Boston Creek | 43.022 | −79.949 | 168 | 15 | 1.8 | 1.7 | 64.1 | 25.0 | 0.0 |
| MR1 | Moira River | 44.478 | −77.468 | 530 | 8 | 1.7 | 3.8 | 6.5 | 71.0 | 0.2 |
| MR2 | Black River | 44.540 | −77.369 | 428 | 2 | 0.7 | 5.2 | 1.5 | 80.0 | 0.0 |
| MR3 | Skootamotta River | 44.549 | −77.328 | 680 | 2 | 0.7 | 8.5 | 0.3 | 79.9 | 0.0 |
| MV1 | South Maitland River | 43.685 | −81.541 | 373 | 9 | 1.8 | 6.0 | 89.0 | 8.0 | 0.0 |
| NP1 | Welland River | 42.972 | −79.318 | 769 | 25 | 2.2 | 4.7 | 70.4 | 20.1 | 0.0 |
| PE1 | Consecon Creek | 43.996 | −77.518 | 187 | 13 | 1.6 | 1.5 | 30.5 | 12.1 | 0.0 |
| SC1 | Sydenham River | 42.831 | −81.851 | 707 | 34 | 1.9 | 7.4 | 83.0 | 13.9 | 0.6 |
| SR1 | Salmon River | 44.196 | −77.229 | 907 | 7 | 1.3 | 10.9 | 8.7 | 58.4 | 0.1 |
| SV1 | Teeswater River | 44.153 | −81.286 | 534 | 9 | 1.6 | 11.1 | 66.2 | 22.4 | 0.0 |
| TR1 | Rouge River | 43.811 | −79.160 | 213 | 1311 | 4.3 | 1.6 | 58.5 | 9.7 | 23.4 |
| UT1 | Dingman Creek | 42.914 | −81.314 | 136 | 459 | 4.3 | 1.5 | 74.5 | 8.8 | 15.4 |
| UT2 | North Thames River | 43.451 | −81.207 | 313 | 22 | 1.9 | 4.5 | 93.6 | 4.7 | 0.7 |
| UT3 | Middle Thames River | 43.031 | −80.998 | 277 | 16 | 2.3 | 3.8 | 87.9 | 10.6 | 0.0 |
| UT4 | South Thames River | 43.019 | −80.927 | 553 | 108 | 2.7 | 5.9 | 84.8 | 9.9 | 3.0 |

$\alpha = 0.05$. Summary statistics were calculated by site and season for data collected between 2005 and 2009 inclusive to compare contemporary chloride concentrations within and amongst watersheds. The Shapiro–Wilk test was used to test for normality of datasets prior to correlation, regression and trend analyses. The non-parametric Spearman rank order correlation on untransformed data was used in initial examinations of bivariate relationships among median and maximum warm season chloride concentrations and watershed attributes (e.g. road density). Because of multicollinearity among the variables, forward stepwise regression analyses were used to generate separate explanatory models for median and maximum warm season chloride concentrations. Only variables having statistically significant effects were retained in the models. Prior to regression, variable data were $\log_{10}$-transformed, with the exception of percent urban which was $\log_{10} + 1$-transformed. Frequency of exceedance curves were developed for the combined data from the 24 sites (1975–2009) to estimate the proportion of time stream water chloride exceeded a given concentration. The non-parametric Mann–Kendall test for monotonic trend (Hirsch et al., 1982) was applied to the May–October results for the period 1975–2009 to assess changes in chloride concentration over time. The trend slope, expressed as change in chloride concentration per year, was estimated using the non-parametric Sen's method (Sen, 1968). Simple linear regression was used to explore the association between warm season chloride concentrations and road salt use.

## 3. Results

### 3.1. Land use influences

Land cover in the watersheds draining to the study sites was dominated by agriculture, ranging from <1 to 94% (median 70%) (Table 1). Forested land cover was the next most prevalent, ranging from 6 to 80% (median 13%). With the exception of the Rouge River (23% urban) and Dingman Creek (15% urban), urban land cover was ≤3%. Population density ranged from 2 to 1311 people $km^{-2}$ (median 20 people $km^{-2}$) and road density ranged from 0.7 to 4.3 km $km^{-2}$ (median 1.9 km $km^{-2}$). Median and maximum warm season chloride concentrations among the 24 sites ranged from 2 to 159 mg $L^{-1}$ (grand median = 29 mg $L^{-1}$) and 4 to 261 mg $L^{-1}$, respectively (Table 2), and were positively correlated with road density, population density, percent agriculture and percent urban and negatively correlated with percent forest (Spearman rank order correlation) (Table 3). Forward stepwise multiple regressions identified road density as the factor that best explained the variation in median (df = 23; F = 119; $p$ <0.001) and maximum (df = 23; F = 40; $p$ <0.001) warm season chloride concentration. No other variables had significant effects in the models. Road density explained 86% and 66% of the variation in median and maximum warm season chloride concentrations (Fig. 2).

### 3.2. Seasonal variability

Frequency analysis for the combined data (1975–2009) from the 24 study sites showed that chloride concentrations ranging from 4 to 90 mg $L^{-1}$, representing 89% of all chloride measurements, were observed more frequently in the warm season than the cold season (Fig. 3). CCME (2011) water quality guidelines for the protection of aquatic life are 640 mg $L^{-1}$ for acute (short-term benchmark) and 120 mg $L^{-1}$ for chronic (long-term exposure guideline) chloride exposure. In the sites examined, 0% and 3.1% of chloride measurements exceeded the acute benchmark and 0.2% and 3.6% exceeded the chronic guideline in the warm and cold seasons, respectively (Fig. 3). However, CCME (2011) cautioned that the chronic guideline may not be sufficiently protective of glochidia of certain mussel species at risk in southern Ontario.

Maximum chloride concentrations occurred in the warm and cold seasons at 10 (42%) and 14 (58%) of the 24 sites, respectively (Table 2). Concentrations peaked in February at sites with relatively high road density (>2 km $km^{-2}$) and between July and October at sites with relatively low road density (<2 km $km^{-2}$) (Fig. 4). In watersheds with relatively low road density, the average monthly maximum chloride concentration in the warm season (172 mg $L^{-1}$) was more than double that of the cold season (84 mg $L^{-1}$).

### 3.3. Long-term trends

Warm season chloride concentrations increased significantly between 1975 and 2009 at 23 of 24 long-term monitoring sites (Mann–Kendall trend test) (Table 2). Rates of increase at sites with a significant trend ranged from 0.02 to 2.8 mg Cl $L^{-1}$ $year^{-1}$ (median 0.4 mg Cl $L^{-1}$ $year^{-1}$). The two most urbanized watersheds, Rouge River and Dingman Creek, at 23% and 15% urban land cover, showed the greatest rate of increase in chloride at ≥2.7 mg Cl $year^{-1}$ (Fig. 5). The Black and Skootamotta Rivers, with the greatest forest cover

**Table 2**
Summary statistics and Mann–Kendall trend test results for stream water chloride concentrations at the study sites.

| Site # | Maximum chloride (mg $L^{-1}$) (1975–2009) | | Warm Season chloride (mg $L^{-1}$) (2005–2009) | | | | Mann–Kendall trend test results (1975–2009) | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Maximum | Date | $n$ | Minimum | Median | Maximum | $n$ | tau | $p$ | Trend slope (mg Cl $L^{-1}$ $year^{-1}$) |
| AB1 | 58 | Nov 1989 | 28 | 19 | 26 | 33 | 187 | 0.41 | <0.001 | 0.3 |
| AB2 | 230 | Aug 1977 | 28 | 20 | 74 | 192 | 174 | 0.24 | <0.001 | 0.5 |
| AB3 | 68 | Oct 1989 | 29 | 21 | 27 | 48 | 176 | 0.43 | <0.001 | 0.4 |
| CR1 | 145 | Oct 1987 | 26 | 14 | 23 | 41 | 127 | 0.08 | 0.165 | |
| GR1 | 850 | Feb 1977 | 29 | 21 | 25 | 42 | 198 | 0.60 | <0.001 | 0.4 |
| GR2 | 55 | Mar 1995 | 29 | 17 | 23 | 31 | 173 | 0.61 | <0.001 | 0.4 |
| GR3 | 74 | Nov 1994 | 28 | 22 | 41 | 60 | 194 | 0.65 | <0.001 | 0.8 |
| GR4 | 326 | Feb 2004 | 29 | 31 | 56 | 181 | 191 | 0.60 | <0.001 | 1.1 |
| GR5 | 64 | Mar 2003 | 11 | 28 | 32 | 47 | 168 | 0.71 | <0.001 | 0.7 |
| GR6 | 83 | Sep 2005 | 11 | 27 | 44 | 83 | 168 | 0.50 | <0.001 | 0.8 |
| MR1 | 22 | Dec 1998 | 28 | 9 | 11 | 14 | 162 | 0.49 | <0.001 | 0.2 |
| MR2 | 8 | Aug 2000 | 28 | 1 | 2 | 4 | 103 | 0.25 | <0.001 | 0.0 |
| MR3 | 19 | Aug 2000 | 28 | 1 | 3 | 13 | 131 | 0.41 | <0.001 | 0.0 |
| MV1 | 36 | Mar 1995 | 28 | 8 | 17 | 23 | 154 | 0.38 | <0.001 | 0.2 |
| NP1 | 111 | Jun 2004 | 29 | 15 | 34 | 110 | 121 | 0.26 | <0.001 | 0.4 |
| PE1 | 47 | Mar 1976 | 19 | 8 | 10 | 15 | 80 | 0.41 | <0.001 | 0.2 |
| SC1 | 58 | Aug 2007 | 29 | 27 | 40 | 58 | 154 | 0.74 | <0.001 | 0.9 |
| SR1 | 27 | Nov 1991 | 29 | 6 | 8 | 16 | 154 | 0.23 | <0.001 | 0.1 |
| SV1 | 40 | Dec 2002 | 33 | 12 | 22 | 33 | 159 | 0.30 | <0.001 | 0.2 |
| TR1 | 765 | Feb 1985 | 28 | 92 | 159 | 224 | 160 | 0.50 | <0.001 | 2.8 |
| UT1 | 1300 | Feb 2000 | 27 | 62 | 134 | 184 | 192 | 0.59 | <0.001 | 2.7 |
| UT2 | 261 | Oct 2007 | 27 | 19 | 58 | 261 | 193 | 0.48 | <0.001 | 1.0 |
| UT3 | 98 | Aug 1999 | 27 | 28 | 35 | 61 | 189 | 0.48 | <0.001 | 0.6 |
| UT4 | 179 | Mar 1993 | 15 | 61 | 87 | 117 | 143 | 0.47 | <0.001 | 1.5 |

(80%) and lowest road density (0.7 km $km^{-2}$) and urban cover (0%), showed the lowest rate of increase at $\leq$ 0.05 mg Cl $year^{-1}$.

Responsibility for winter road maintenance is divided between the Ministry of Transportation of Ontario (MTO), which is responsible for the maintenance of 16 500 km of provincial highways, and the municipalities which manage the secondary roads within their respective jurisdictions. Long-term road salt use data for the municipalities in the study watersheds were not available. Data from MTO were used as a surrogate for total road salt use in Ontario. Simple linear regression showed that 36% of the variation in annual median warm season chloride concentration for the study sites was explained by amount of road salt used by MTO in the previous winter (Fig. 6).

## 4. Discussion

### 4.1. Effects of road salt use on water quality in mussel habitats

Many factors have contributed to mussel declines including habitat loss, water contamination, declines in host species and introductions of invasive species (Strayer et al., 2004). Dramatic declines in native freshwater mussels in the Great Lakes and their interconnecting channels have been attributed to the invasion of dreissenid (zebra and quagga) mussels (Schloesser and Nalepa, 1994; Schloesser et al., 2006). Streams draining into the Great Lakes have not been colonized to the same extent by the invasive dreissenid mussels, leaving these streams as last refuges for many native mussel species (Metcalfe-Smith et al., 1998). Water quality is an important factor in the conservation of native mussels in these refuge habitats. Metcalfe-Smith et al. (2000) reported a rebound in the mussel population of the Grand River since the early 1970s which they attributed to improvements in water quality; however, they expressed concern that the growing pressures of land development in the region could halt or reverse improvements in water quality and gains in mussel recovery. Ontario's population is projected to increase by 34% between 2010 and 2036, with the bulk of this projected growth in southern Ontario (Ontario Ministry of Finance, 2011).

Significant correlations between stream chloride concentrations and varying measures of watershed development indicate an anthropogenic source of chloride loading. In northeastern North America, road salt has been identified as the largest contributor to stream chloride loading (Mayer et al., 1999; Kaushal et al., 2005); however, wastewater effluent can be an important source of chloride loading in selected urban watersheds (Novotny et al., 2009). Data cited in CCME (2011) indicate that the estimated annual chloride loading from road salt (1 148 570 tonnes) is over six times greater than the estimated loading from wastewater effluent (175 000 tonnes) in Ontario. Chloride loading from other possible sources, including calcium chloride dust suppressants, is assumed

**Table 3**
Spearman rank order correlations between warm season chloride concentrations and watershed attributes at the study sites.

| | Median chloride | Maximum chloride | Population density | Road density | Mean flow | Agriculture | Forest | Urban |
|---|---|---|---|---|---|---|---|---|
| Median chloride | 1.00 | | | | | | | |
| Maximum chloride | **0.96** | 1.00 | | | | | | |
| Population density | **0.78** | **0.72** | 1.00 | | | | | |
| Road density | **0.83** | **0.78** | **0.86** | 1.00 | | | | |
| Mean flow | −0.35 | −0.37 | −0.12 | −0.15 | 1.00 | | | |
| Agriculture | **0.52** | **0.52** | 0.40 | **0.55** | 0.07 | 1.00 | | |
| Forest | **−0.58** | **−0.57** | **−0.46** | **−0.60** | 0.18 | **−0.89** | 1.00 | |
| Urban | **0.67** | **0.57** | **0.68** | **0.64** | −0.05 | 0.29 | **−0.43** | 1.00 |

Absolute values of Spearman correlations >0.407 are significant at $\alpha = 0.05$ and shown in bold. The Bonferroni correction for evaluating 28 correlations simultaneously increases the critical value for the correlation to 0.476.

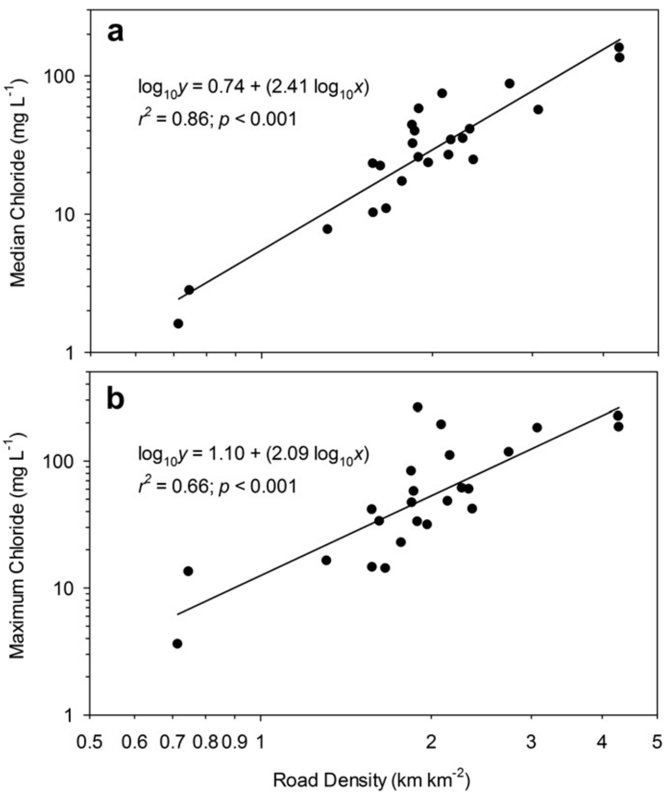


**Fig. 2.** Regressions of (a) Median and (b) Maximum warm season chloride concentrations versus road density at the 24 study sites.

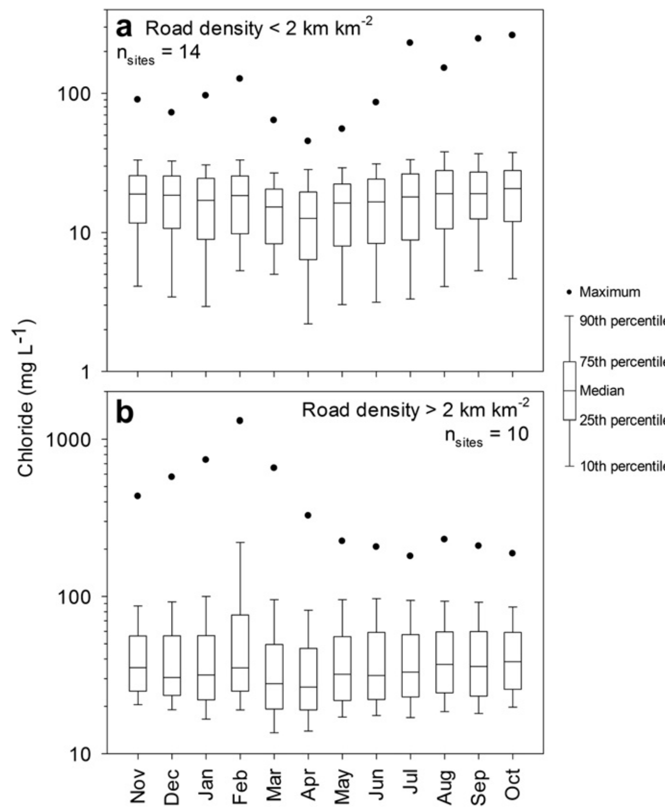


**Fig. 4.** Monthly stream water chloride concentrations (1975–2009) for study sites with road density (a) < 2 km km$^{-2}$ and (b) > 2 km km$^{-2}$.

to be minor in comparison to road salt. Morin and Perchanok (2003) estimated that calcium chloride dust suppressant and sodium chloride road salt comprised <3% and >97% of the amount of chloride applied to Ontario roads annually.

Many Ontario road authorities have developed plans to better manage road salt use to reduce the environmental impacts of chloride while maintaining road safety; however, less attention has been paid to identifying areas within the recipient ecosystems that are vulnerable to salt loading (Stone and Marsalek, 2011). Findlay and Kelly (2011) suggest that sessile organisms in close proximity to salted roads will be affected most quickly and to the greatest extent, with beds of freshwater mussels in streams being particularly vulnerable. Stream habitats of mussel species at risk in Ontario

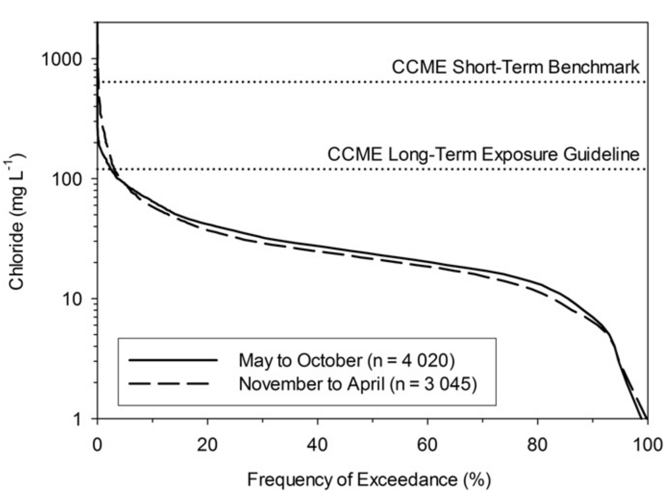


**Fig. 3.** Frequency analysis for stream water chloride concentrations at the 24 study sites during the warm (May to October) and cold (November to April) seasons from 1975 to 2009. Canadian Council of Ministers of the Environment (CCME, 2011) Water quality guidelines for the protection of aquatic life for acute (short-term benchmark) and chronic (long-term exposure guideline) chloride exposure are shown by the horizontal dashed lines.

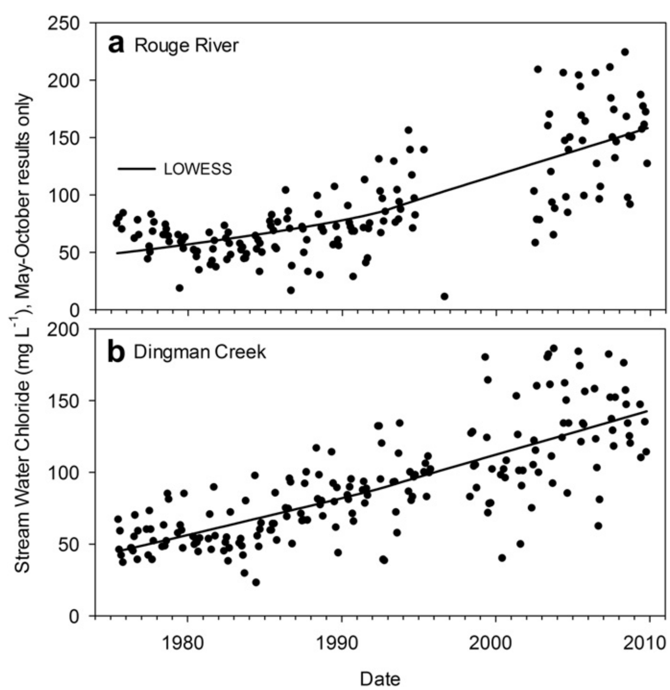


**Fig. 5.** Stream water chloride concentration (May–October results only) versus time for the most urbanized of the monitoring sites (a) Rouge River and (b) Dingman Creek. LOWESS = locally weighted scatterplot smooth.

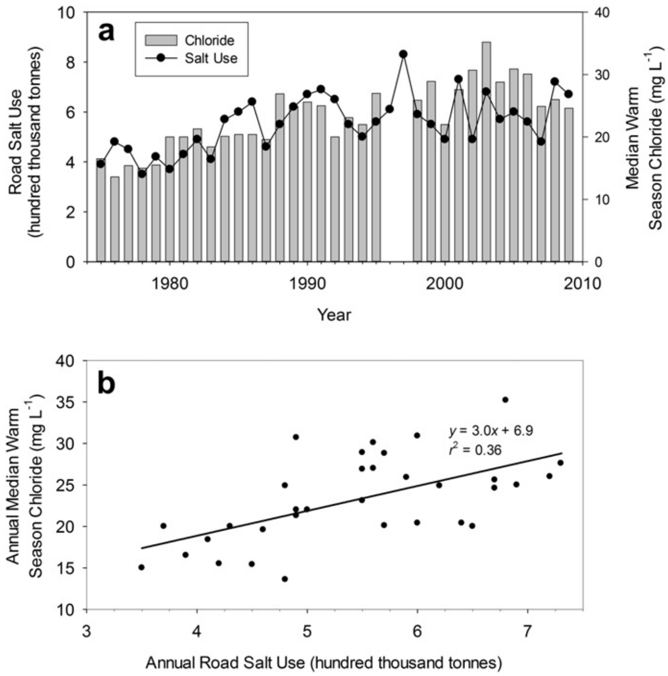


**Fig. 6.** (a) Amount of road salt applied per winter by the Ministry of Transportation of Ontario (where 1975 reflects the amount for winter 1974–75 and so on) with the annual median warm season chloride concentration across 24 independent mussel habitats. Medians for 1996 and 1997 were omitted due to reductions in monitoring in those years. Road salt use estimates are from Perchanok (2010). (b) Annual median warm season chloride concentration versus annual road salt use.

have been mapped (Fisheries and Oceans Canada, 2011). The intersections of salted roads and these critical stream habitats represent potentially vulnerable areas where road authorities might consider the need for additional salt management measures. Results from this study could be used to further refine the identification of vulnerable areas. The results show areas where contemporary chloride concentrations exceed or are approaching levels shown to be toxic to glochidia in laboratory studies, and areas where concentrations are increasing at a rate that indicates potential for future impacts.

### 4.2. *Seasonal variability*

The timing and duration of exposure to elevated stream water chloride concentrations are important considerations in assessing effects on aquatic life. There is greater potential for negative effects if periods of elevated chloride overlap with sensitive life stages. The release of glochidia in the warm season would seem to favour mussel reproduction given that peak stream water chloride concentrations typically coincide with road salt application and surface runoff (Perera et al., 2009; Corsi et al., 2010; Gardner and Royer, 2010). However, peak concentrations in 42% of the streams in the current study occurred in the warm season. Frequency analyses also showed that chloride concentrations were routinely higher in the warm season compared to the cold season. These results show that warm season chloride concentrations can remain elevated after snow melt and flushing with spring rains, and that peak concentrations can occur several months after the last application of road salt. This suggests a release of chloride from groundwater or other subsurface storage.

The exact mechanisms of road salt retention in the study watersheds are unknown. It is possible that the warm season peaks are the result of summer storms flushing chloride from the shallow subsurface into streams during low flow periods when the dilution potential is minimal. Meriano et al. (2009) reported that approximately 30% of the chloride that was removed annually by surface runoff was flushed from the Pine Creek watershed in the warm season. Warm season peaks could also be explained by increased discharge of contaminated groundwater. Rosenberry et al. (1999) observed that reduced evapotranspiration and increased recharge in the fall (October–November) caused a reversal of the hydraulic gradient between a stream and the underlying groundwater such that some of the chloride stored beneath the streambed was flushed into the stream. This phenomenon might explain why chloride concentrations peaked in October at several of the study sites.

The study results also suggest that seasonal variability in chloride is influenced by the level of watershed development. A greater than 5-fold difference between cold and warm season maximum chloride concentrations was observed in the watersheds with relatively high road density whereas an approximately 2-fold difference was observed in watersheds with low road density. Concentrations peaked in the cold season at sites with higher road density and in the warm season at sites with lower road density. These results suggest higher rates of chloride retention in less developed watersheds such that cold season peaks in chloride concentration are dampened and warm season concentrations are elevated.

### 4.3. *Long-term trends*

Significant increasing trends in warm season chloride concentrations in 96% (23/24) of mussel habitats reflect decades of increasing road salt use and retention. Road salt has been used for winter road de-icing in Canada since the 1940s and its use in terms of total mass and per length of road has increased since record keeping began in the early 1960s (Morin and Perchanok, 2003). Morin and Perchanok (2003) estimated that road salt use by the Ministry of Transportation of Ontario, one of the largest road salt users in Ontario, increased from approximately 400 000 tonnes in winter 1974–75 to approximately 600 000 tonnes in winter 1997–98 (an increase of approximately 2% per year), and from <10 tonnes per 2-lane km in winter 1978–79 to >25 tonnes per 2-lane km in winter 1997–98 (an increase of approximately 8% per year). Simple linear regression showed that 36% of the variation in warm season chloride concentrations at the study sites was explained by amount of road salt used by the provincial transportation ministry in the previous winter. This suggests that reductions in the amount of road salt applied in a given winter should result in lower stream water chloride concentrations in the following summer. However, with retention of chloride in soils and groundwater, stream chloride concentrations may continue to increase even if salt input decreases or ceases (Kelly et al., 2008).

Rates of change in the mostly rural streams in the current Ontario-based study are consistent with studies of rural streams in neighbouring New York State. Godwin et al. (2003) showed that chloride concentrations in the Mohawk River (<6% urban land cover) increased by 19.9 mg $L^{-1}$ from 1952 to 1998, which equates to an approximately 0.4 mg $L^{-1}$ $year^{-1}$ increase, and Kelly et al. (2008) observed a 1.5 mg $L^{-1}$ $year^{-1}$ increase in mean annual chloride concentration in East Wappinger Creek (9% urban land cover) from 1986 to 2005 despite the fact that road salt use did not increase over the same time period. Winter et al. (2011) similarly observed that rates of change in stream water chloride concentrations varied with the level of watershed development in tributaries to Lake Simcoe, Ontario. They reported increases ranging from 0.6 to 1.4 mg Cl $L^{-1}$ $year^{-1}$ in six watersheds with 2–6% urban land cover and increases of 5.2 and 10.4 mg Cl $L^{-1}$ $year^{-1}$ in two watersheds with 26 and 27% urban land cover. These results suggest that increased urban development is likely to accelerate the rate of increase in stream water chloride concentrations.

Perera et al. (2009) estimate that, from 1995 to 2007, the normalized salt application rates in the City of Toronto, a leader in best salt management practices in Ontario, declined from 0.08 to 0.07 tonnes of salt applied per centimetre of snowfall per kilometre of road lane. This suggests that efforts to reduce salt use may be effective; however, increased urbanization with population growth increases the area of roads and parking lots that require winter maintenance, counteracting efforts to reduce salt use. Another confounding factor is the uncertain influence of climate change. For example, in the Lake Erie region of the Great Lakes basin, Kunkel et al. (2002) predicted warmer winter air temperatures and a reduction in weather conditions favourable for heavy lake-effect snow in the late 21$^{st}$ century. The influences of changes in the frequency and severity of winter weather on road salt application and the transport of chloride in the environment are uncertain. It is possible that milder winter temperatures will result in more freeze-thaw cycles requiring additional road salt applications, or less salt may be required if there are fewer heavy snow storms.

Gillis (2011) reported 24-h EC20 concentrations ranging from 153 to 432 mg Cl $L^{-1}$ for glochidia of the wavy-rayed lampmussel (*Lampsilis fasciola*) using salt-spiked water samples from mussel habitats in southern Ontario. These concentrations reflect the level of chloride exposure that was acutely toxic to 20% of glochidia in laboratory studies. Warm season concentrations exceeding 153 mg Cl $L^{-1}$ were measured at several of the sites in the current study indicating that acute toxicity is possible at present day concentrations. Of potentially greater concern are the long-term increases in warm season concentrations and the projections for continued development of southern Ontario. If chloride were to continue to increase at the rates identified in Table 2, assuming no change in rate of road salt application or level of watershed development, median warm season chloride concentrations in 21% (5/24) of the study sites would exceed 153 mg Cl $L^{-1}$ in the next century. However, given the projected 34% increase in the population of Ontario over the next 25 years, it is likely that levels of watershed development and amounts of road salt applied will increase and that the proportion of study sites reaching potentially toxic levels of chloride will be even higher.

This paper focussed on stream habitats of freshwater mussels because of their demonstrated sensitivity to chloride in comparison to other aquatic species. It should be noted, however, that increases in stream water chloride concentrations have the potential to impact other sensitive species such as amphibians (Karraker et al., 2008) and benthic macroinvertebrates (Williams et al., 1997). It is also possible that chloride could interact with other contaminants (e.g. copper, cadmium, pesticides) to have less-recognized cumulative effects on glochidia, other mussel life stages, or other sensitive aquatic species.

## 5. Conclusions

Seasonal and long-term trends suggest that a portion of the chloride loading from road salt is being retained in southern Ontario watersheds, resulting in a gradual increase in baseline stream water chloride concentrations over seasons and years. Given the trend towards higher exposure levels in the warm season, and the sensitivity of glochidia to chloride, recovery strategies for freshwater mussels should consider the likelihood of existing and future negative effects from road salting.

## Acknowledgements

The authors are grateful to Ontario's Conservation Authorities for sample collection, the Laboratory Services Branch of the Ontario Ministry of the Environment for sample analysis, and S. Sunderani and C. Rocks for their assistance in data management. Reviews by P. Goel, M. Mohamed, J. Thomas and two anonymous reviewers resulted in improvements to earlier drafts of this manuscript.

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